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(54) TONER BINDER

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## (57)Abstract:

PROBLEM TO BE SOLVED: To obtain a toner binder excellent in both low temp. fixability and anti-hot-offsetting property, having an appropriate quantity of electric charges, excellent also in environmental stability and giving a dry toner.

SOLUTION: A polycondensation resin (A) and other resin (B) are combined so as to attain a dielectric tangent ( $\tan \delta$ ) satisfying the relation of  $\text{Log}(\tan \delta) = a \times (100 - \text{WA}) + b$  [where WA is the resin A content (wt.%) of the resultant combined resin, each of (a) and (b) is a constant,  $a = -0.0068$  and  $b = -2.07$ ].

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**CLAIMS**


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**[Claim(s)]**

[Claim 1] The toner binder characterized by the dielectric dissipation factor (tandelta) in the content (WA % of the weight) of (A) in the resin (alpha) which compound[ this ]-ized in the toner binder which consists of resin (alpha) which compound-ized polycondensation system resin (A) and other resin (B), and 100kHz of test frequencies of (alpha) being the relation of a formula (1).

$$\text{Log(tandelta)} \leq a \times (100 - \text{WA}) + b \quad (1)$$

(a and b are constants among a formula and it is  $a = -0.0068$  and  $b = -2.07$ )

[Claim 2] The toner binder characterized by the content (WA % of the weight) of (A) in the resin (alpha) which compound[ this ]-ized in the toner binder which consists of resin (alpha) which compound-ized polycondensation system resin (A) and other resin (B), the dielectric dissipation factor (tandelta) in 100kHz of test frequencies of (alpha), and the glass transition point (Tg) of (alpha) being the relation of a formula (2).

$$\text{Log(tandelta)} \leq \{a - m \times (Tg - n)\} \times (100 - \text{WA}) + b \quad (2)$$

(a, b, m, and n are constants among a formula, and it is  $a = -0.0068$ ,  $b = -2.07$ ,  $m = 0.00030$ , and  $n = 60$ )

[Claim 3] The toner binder according to claim 1 or 2 whose \*\* (WA) is 10 - 90 % of the weight.

[Claim 4] Claims 1-3 whose \*\* (A) are amorphous polyester are the toner binders of a publication either.

[Claim 5] Claims 1-4 whose \*\* (B) are vinyl system resin (B1) are the toner binders of a publication either.

[Claim 6] The toner binder according to claim 5 whose \*\* (B1) is styrene resin.

[Claim 7] Claims 1-6 whose \*\* (alpha) are resin in which a part of \*\* (A) and \*\* [ at least ] (B) carried out the chemical bond are the toner binders of a publication either.

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**TECHNICAL FIELD**

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[Field of the Invention] This invention relates to the toner binder for dry type toners used for electrophotography, electrostatic recording, electrostatic printing, etc.

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PRIOR ART

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[Description of the Prior Art] Conventionally, what carried out melting kneading with the coloring agent etc., and pulverized toner binders, such as styrene acrylic resin and polyester, as a dry type toner used for electrophotography etc. is used. Frictional electrification of these dry type toners is carried out to carriers, such as ferrite powder, or an electrification grant member, and they are developed by the electrostatic latent image formed on the photo conductor in this. Subsequently, after imprinting on paper etc., being established by carrying out heating fusion using a hot calender roll is performed. In that case, in order to develop negatives by sufficient image concentration, it is required to have the proper amount of electrifications. Moreover, in any temperature and humidity, it is called for that the difference of the amount of electrifications is small (environmental stability). Furthermore, in the fixing side, a toner does not weld to a hot calender roll at hot calender roll temperature still higher than before from a viewpoint of a miniaturization of equipments, such as energy saving and a copying machine, (hot-proof offset nature), and even if hot calender roll temperature is low, it is called for that a toner can be established (low-temperature fixable). Since it excels in low-temperature fixable one and hot-proof offset nature in recent years, its attention is paid to the toner binder of a polyester system. However, the toner using a polyester system toner binder has a problem with the inadequate environmental stability of electrification. Furthermore, in the magnetic toner containing magnetic powder, the problem from which image concentration with it is not obtained has arisen. [ the low amount of electrifications and ] [ sufficient ] In the small developer especially used for a printer etc., the problem that this amount of electrifications is insufficient is remarkable.

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**EFFECT OF THE INVENTION**

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[Effect of the Invention] The toner binder of this invention does the following effectiveness so.

1. When it is made a dry type toner, the amount of electrifications is proper, and excel in environmental stability. The amount of electrifications at the time of making it a magnetic toner is especially high, and image concentration is high.
2. Excel in both low-temperature fixable one and hot-proof offset nature.
3. It excels in endurance and after a long-term copy has little degradation of an image.

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**TECHNICAL PROBLEM**

[Problem(s) to be Solved by the Invention] The approaches (for example, JP,62-195682,A, JP,2-881,A, JP,4-142301,A, etc.) of compound-izing dominance styrene acrylic resin in polyester in an electrification property as what solves the problem of the amount of electrifications of the above-mentioned polyester system toner binder and environmental stability are proposed. however, what is indicated by these only has the in-between property of polyester and styrene acrylic resin, although the amount of electrifications and environmental stability improve rather than conventional polyester -- \*\*\*\* -- it does not pass but an electrification property is inferior to styrene acrylic resin. Furthermore, the description of polyester is halved also about low-temperature fixable one and hot-proof offset nature.

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MEANS

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[Means for Solving the Problem] this invention persons reached this invention, as a result of inquiring wholeheartedly that the toner binder which was excellent in both low-temperature fixable one and hot-proof offset nature, and whose amount of electrifications was proper and was excellent in environmental stability and which gives a dry type toner should be developed. That is, this invention is a toner binder characterized by the dielectric dissipation factor (tandelta) in the content (WA % of the weight) of (A) in the resin (alpha) which compound[ this ]-ized in the toner binder which consists of resin (alpha) which compound-ized polycondensation system resin (A) and other resin (B), and 100kHz of test frequencies of (alpha) being the relation of a formula (1).

$$\text{Log(tandelta)} \leq ax(100-WA) + b \quad (1)$$

(a and b are constants among a formula and it is  $a = -0.0068$  and  $b = -2.07$ )

[0005]

[Embodiment of the Invention] Hereafter, this invention is explained in full detail. In this invention, polyester (A1), a polyamide (A2), polyurethane (A3), a polycarbonate (A4), a polyester polyamide (A5), polyester polyurethane (A6), etc. are mentioned as polycondensation system resin (A). Things desirable [ among these ] are (A1), (A5), and (A6), a still more desirable thing is (A1), and especially a desirable thing is amorphous polyester. The polycondensation object of polyol and polycarboxylic acid etc. is mentioned as (A1). As polyol, diol (1) and the polyol more than trivalent (2) are mentioned, and dicarboxylic acid (3) and the polycarboxylic acid more than trivalent (4) are mentioned as polycarboxylic acid. In this invention, the polyester [ dicarboxylic acid / diol (1) and / (3) ] of a non-line using the polyol more than trivalent (2) and/or the polycarboxylic acid more than trivalent (4) is desirable, and especially the polyester that consists of four components of (1), (2), (3), and (4) is desirable. Hot-proof offset nature improves more by using both (2) and (4).

[0006] as diol (1) -- alkylene glycol (ethylene glycol --) 1, 2-propylene glycol, 1, 3-propylene glycol, 1,4-butanediol, ; alkylene ether glycols (a diethylene glycol --), such as 1,6-hexanediol and dodecane diol Triethylene glycol, dipropylene glycol, a polyethylene glycol, ; alicyclic diols (1 and 4-cyclohexane dimethanol --), such as a polypropylene glycol and a polytetramethylene ether glycol ; bisphenols (bisphenol A --), such as hydrogenation bisphenol A and the hydrogenation bisphenol F the alkylene oxide (ethyleneoxide --) of the; above-mentioned alicyclic diol, such as Bisphenol F and Bisphenol S Propylene oxide, butylene oxide, styrene oxide, Addition products, such as alpha olefin oxide; the alkylene oxide (ethyleneoxide, propylene oxide, butylene oxide, styrene oxide, alpha olefin oxide, etc.) addition product of the above-mentioned bisphenols etc. is mentioned. Things desirable [ among these ] are with a carbon numbers of six or more alkylene glycol, the alkylene oxide addition product of bisphenols, and alicyclic diol, and especially desirable things are the propylene oxide of bisphenols, butylene oxide, styrene oxide, an alpha olefin oxide addition product, with a carbon numbers of eight or more alkylene glycol, hydrogenation bisphenol A, the hydrogenation bisphenols F, and these concomitant use. As polyol more than trivalent (2), the alkylene oxide addition product of the alkylene oxide addition product; above-mentioned novolak resin of 3 - 8 \*\* or the multiple-valued fatty alcohol (glycerol, trimethyloethane, trimethylol propane, pentaerythritol, sorbitol,

etc.); tris phenols (tris phenol PA etc.); novolak resin (phenol novolak, cresol novolak, etc.); above-mentioned tris phenols beyond it etc. is mentioned. Things desirable [ among these ] are 3 - 8 \*\* or the multiple-valued fatty alcohol beyond it, and the alkylene oxide addition product of novolak resin, and especially a desirable thing is the alkylene oxide addition product of novolak resin.

[0007] As dicarboxylic acid (3), alkylene dicarboxylic acid (succinic-acid, adipic-acid, azelaic-acid, sebacic-acid, dodecane dicarboxylic acid, OKUTA decane dicarboxylic acid, dodecenyl succinic-acid, PENTA decenyl succinic-acid, octadecenyl succinic-acid, dimer acid, etc.); ARUKENI range carboxylic-acids (maleic-acid, boletic acid, etc.); aromatic series dicarboxylic acid (a phthalic acid, isophthalic acid, a terephthalic acid, naphthalene dicarboxylic acid, etc.) etc. is mentioned. A thing desirable [ among these ] The alkylene dicarboxylic acid of carbon numbers 6-50, They are the ARUKENI range carboxylic acid of carbon numbers 6-50, the aromatic series dicarboxylic acid of carbon numbers 8-20, and these concomitant use. A still more desirable thing It is concomitant use of the alkylene dicarboxylic acid of carbon numbers 7-50, and the aromatic series dicarboxylic acid of these and carbon numbers 8-20, and especially a desirable thing is concomitant use of the alkenyl succinic acid of carbon numbers 16-50, and the aromatic series dicarboxylic acid of these and carbon numbers 8-20. As polycarboxylic acid more than trivalent (4), the vinyl polymerization objects (styrene / maleic-acid copolymerization object, styrene / acrylic-acid copolymerization object, an alpha olefin / maleic-acid copolymerization object, styrene / fumaric-acid copolymerization object, etc.) of the aromatic polycarboxylic acids of carbon numbers 9-20 and unsaturated carboxylic acid (trimellitic acid, pyromellitic acid, etc.) etc. are mentioned. Things desirable [ among these ] are the aromatic polycarboxylic acids of carbon numbers 9-20, and especially a desirable thing is trimellitic acid. In addition, as dicarboxylic acid (3) or polycarboxylic acid more than trivalent (4), the above-mentioned acid anhydride or the low-grade alkyl ester of a thing (methyl ester, ethyl ester, isopropyl ester, etc.) may be used.

[0008] Moreover, hydroxycarboxylic acid (5) can also be copolymerized with (1), (2), (3), and (4). As hydroxycarboxylic acid (5), hydroxy stearin acid, a hydrogenated-castor-oil fatty acid, etc. are mentioned.

[0009] the ratio of polyol and polycarboxylic acid -- as equivalent ratio  $[OH]/[COOH]$  of a hydroxyl group  $[OH]$  and a carboxyl group  $[COOH]$  -- usually --  $2 / 1 - 1/2$  -- desirable --  $1.5 / 1 - 1/1.5$  -- it is  $1.3 / 1 - 1/1.3$  still more preferably. the ratio of the polyol more than trivalent (2), and the polycarboxylic acid more than trivalent (4) -- the mol of (2) and (4) -- the sum of a number -- the mol of (1) - (4) -- the sum total of a number -- receiving -- usually -- 0 - 40-mol % -- desirable -- 3 - 25-mol % -- it is 5 - 20-mol % still more preferably. the mole ratio of (2) and (3) -- usually -- 0 / 100 - 100/0 -- desirable -- 80 / 20 - 20/80 -- it is 70 / 30 - 30/70 still more preferably.

[0010] 40 or less mgKOH/g of hydroxyl values of (A1) is 70 or less mgKOH/g usually 30 or less mgKOH/g still more preferably preferably. The one where a hydroxyl value is smaller is desirable at the point environmental stability and whose amount of electrifications improve. The acid number of (A1) is usually 8 - 25 mgKOH/g especially preferably eight to 30 mgKOH/g still more preferably five to 50 mgKOH/g preferably zero to 50 mgKOH/g. Although environmental stability of the one where the acid number is smaller improves, the way which has the moderate acid number is desirable at the point whose standup of electrification improves.

[0011] As a polyester polyamide (A5), (1) - (5) which constitutes the above (A1), diamine (6) and amino acid (7), or a copolycondensation object with amino alcohol (8) is mentioned. As diamine (6), alkylene diamines (ethylenediamine, hexamethylenediamine, etc.), aromatic series diamines (a phenylenediamine, xylylene diamine, etc.), etc. are mentioned. As amino acid (7), aminopropionic acid, aminocaproic acid, epsilon caprolactam, etc. are mentioned. Ethanolamine etc. is mentioned as amino alcohol (8). The content of (6) - (8) in a polyester polyamide (A5) is usually 1 - 40-mol %, and is 2 - 20-mol % preferably.

[0012] As polyester polyurethane (A6), the urethane ghost of the above (A1) and the poly isocyanate (9) etc. is mentioned. as the poly isocyanate (9) -- aliphatic series poly isocyanate (tetramethylene di-isocyanate --); alicyclic poly isocyanates (isophorone diisocyanate --), such



as hexamethylene di-isocyanate, 2, and 6-JIISOSHIANATOMECHIRUKAPUROETO ; aromatic series diisocyanate (tolylene diisocyanate --), such as cyclo hexylmethane diisocyanate ; aroma aliphatic series diisocyanate [ , such as diphenylmethane diisocyanate, ] (alpha, alpha, alpha', alpha'-tetramethyl xylylene diisocyanate, etc.); -- isocyanurate; -- said poly isocyanate -- a phenol derivative -- Thing; blocked by the oxime, the caprolactam, etc. and these two or more sorts of concomitant use are mentioned. the ratio of the poly isocyanate (C) -- as equivalent ratio  $[NCO]/[OH]$  of an isocyanate radical  $[NCO]$  and the hydroxyl group  $[OH]$  of polyester -- usually --  $1 / 2 - 2/1$  -- desirable --  $1.5 / 1 - 1/1.5$  -- it is  $1.2 / 1 - 1/1.2$  still more preferably.

[0013] As other resin (B), addition condensation resin, vinyl system resin, polyaddition resin, and polycondensation resin are mentioned. \*\* with vinyl system resin and addition condensation resin desirable [ among these ] and especially vinyl system resin are desirable. As addition condensation resin, xylene resin, a phenol novolak, a cresol novolak, etc. are mentioned, and a thing desirable in these is xylene resin. As vinyl system resin, styrene resin, acrylic resin, polyolefine, the poly cycloalkene, the poly alkenyl cycloalkane, halogenation vinyl resin, etc. are mentioned. A thing desirable [ among these ] is styrene resin. As styrene resin, the polymer (B1) of styrene, the copolymer (B-2) of styrene and dienes, the copolymer (B3) of styrene and alkyl (meta) acrylate, etc. are mentioned. Good better things are the copolymers of the alkyl (meta) acrylate which has (B1), (B-2), styrene, and the alkyl group of C8-C24, and those concomitant use among these. As styrene which constitutes (B1), styrene, alpha methyl styrene, p-methyl styrene, m-methyl styrene, p-methoxy styrene, p-hydroxystyrene, p-acetoxy styrene, etc. are mentioned. A thing desirable [ among these ] is concomitant use of styrene and styrene, and other styrene, and especially a desirable thing is styrene.

[0014] As styrene which constitutes (B-2), the same thing as the above (B1) is mentioned, and the same is said of a desirable thing. As dienes, a butadiene, an isoprene, a chloroprene, hexadiene, OKUTA diene, etc. are mentioned. Things desirable [ among these ] are a butadiene, an isoprene, and a chloroprene, and especially desirable things are a butadiene and an isoprene. In (B-2), little copolymerization of the other monomers can also be carried out with styrene and dienes. As other monomers which can be copolymerized, alkyl (meta) acrylate [methyl (meta) acrylate, Ethyl (meta) acrylate, butyl (meta) acrylate, 2-ethylhexyl (meta) acrylate, ], such as lauryl (meta) acrylate and stearyl (meta) acrylate, Permutation alkyl (meta) acrylate [hydroxyethyl (meta) acrylate, ], such as dimethylaminoethyl (meta) acrylate, unsaturated carboxylic acid, and the anhydride [(meta) acrylic acid of those, ], such as a maleic acid, a fumaric acid, an itaconic acid, and its anhydride, partial saturation dicarboxylic acid alkyl ester [maleic-acid monomethyl, ], such as maleic-acid monobutyl, dibutyl maleate, and itaconic-acid monomethyl, Partial saturation nitril [(meta) acrylonitrile] etc., vinyl ester [vinyl acetate] etc., vinyl ether [butyl vinyl ether] etc., an alpha olefin [a hexene, octene, dodecen], etc., etc. are mentioned. Things desirable [ among these ] are alkyl (meta) acrylate, unsaturated carboxylic acid and the anhydride of those, partial saturation dicarboxylic acid alkyl ester, and partial saturation nitril, and are the long-chain alkyl (meta) acrylate which has the alkyl group of C8-C24, unsaturated carboxylic acid and an anhydride of those, and partial saturation dicarboxylic acid alkyl ester still more preferably. Although tandelta will become large if the monomer of carboxylic-acid content like unsaturated carboxylic acid and the anhydride of those, and partial saturation dicarboxylic acid monoalkyl ester is copolymerized so much, little copolymerization is desirable at the point whose pigment dispersibility improves. For styrene, 60 - 99 % of the weight and dienes is [ the monomer of 1 - 40 % of the weight and others ] 0 - 10 % of the weight, and, for styrene, dienes are [ the other monomers of the copolymerization ratio of other monomers in which styrene, dienes, and copolymerization are possible ] usually 0 - 5 % of the weight five to 30% of the weight 70 to 95% of the weight preferably.

[0015] As styrene which constitutes (B3), the same thing as the above (B1) is mentioned, and the same is said of a desirable thing. As alkyl (meta) acrylate, methyl (meta) acrylate, ethyl (meta) acrylate, butyl (meta) acrylate, 2-ethylhexyl (meta) acrylate, DESHIRU (meta) acrylate, lauryl (meta) acrylate, tetradecyl (meta) acrylate, hexadecyl (meta) acrylate, stearyl (meta) acrylate, behenyl (meta) acrylate, etc. are mentioned. A thing desirable [ among these ] is long-

chain alkyl (meta) acrylate which has the alkyl group of C8-C24, a still more desirable thing is long-chain alkyl (meta) acrylate which has the alkyl group of C12-C22, and especially desirable things are lauryl (meta) acrylate and stearyl (meta) acrylate. In (B3), other monomers can also be copolymerized with styrene and alkyl (meta) acrylate. As other monomers which can be copolymerized, the same thing as the above (B-2) and dienes are mentioned. Things desirable [ among these ] are dienes, unsaturated carboxylic acid and the anhydride of those, partial saturation dicarboxylic acid alkyl ester, and partial saturation nitril, and are dienes, unsaturated carboxylic acid and an anhydride of those, and partial saturation dicarboxylic acid alkyl ester still more preferably. Although  $\tan\delta$  will become large if the monomer of carboxylic-acid content like unsaturated carboxylic acid and the anhydride of those, and partial saturation dicarboxylic acid monoalkyl ester is copolymerized so much, little copolymerization is desirable at the point whose pigment dispersibility improves. For styrene, 70 - 99 % of the weight and alkyl (meta) acrylate is [ the monomer of 1 - 30 % of the weight and others ] 0 - 10 % of the weight, and, for styrene, alkyl (meta) acrylate is [ the other monomers of the copolymerization ratio of other monomers in which styrene, alkyl (meta) acrylate, and copolymerization are possible ] usually 0 - 5 % of the weight five to 20% of the weight 80 to 95% of the weight preferably.

[0016] Although the mixture of the resin (B) of polycondensation system resin (A) and others is sufficient as the resin (alpha) which this invention compound-ized, it can carry out the chemical bond of the (B) to (A).  $\tan\delta$  becomes small and its resin in which a part of (B) carried out the chemical bond to (A) is more desirable at the point environmental stability and whose amount of electrifications improve more. [ at least ] A block copolymer and a graft copolymer are mentioned as resin in which (B) carried out the chemical bond to (A).

[0017] In this invention, the dielectric dissipation factor ( $\tan\delta$ ) in 100kHz of test frequencies of the compound-ized resin (alpha) has the content (WA % of the weight) of inner (alpha) polycondensation system resin (A), and the following relation.

$$\text{Log}(\tan\delta) \leq ax(100-WA) + b \quad (1)$$

(The inside a and b of a formula is a constant)

a -- usually -0.0068 -- it is -- desirable -0.0075 -- further -- desirable -0.0080 -- it is -0.0090 especially preferably. b -- usually -2.07 -- it is -- desirable -2.10 -- further -- desirable -2.22 -- it is -2.26 especially preferably. It is desirable from a viewpoint of coexistence of a fixing property (low-temperature fixable one, hot-proof offset nature) and an electrification property (the amount of electrifications, environmental stability) that  $\tan\delta$  is the above-mentioned range. Furthermore, as for  $\tan\delta$ , it is desirable to have the following relation between WA and a glass transition point ( $T_g$ ).

$$\text{Log}(\tan\delta) \leq [a - mx(T_g - n)] \times (100 - WA) + b \quad (2)$$

(The inside a, b, m, and n of a formula is a constant)

The value of a in a formula (2) and b is the same as that of the case of said formula (1). m is usually 0.00030 and is 0.00040 preferably [ it is desirable and ] to 0.00035 and a pan. n -- usually -- 60 -- desirable -- 57 -- it is 55 still more preferably. It is desirable from a viewpoint of coexistence of low-temperature fixable one and an electrification property (the amount of electrifications, environmental stability) that  $\tan\delta$  is the above-mentioned range. After  $\tan\delta$  carries out melting kneading for 30 minutes and grinds resin subsequently to 20 micrometers or less by 130 degrees C and 70rpm using a lab PURASUTO mill, it carries out compression molding and can be measured by using a commercial dielectric loss measuring device.

[0018] the content (WA) of the polycondensation system resin (A) in the compound-ized resin (alpha) -- usually -- it is 25 - 75 % of the weight still more preferably 20 to 80% of the weight preferably ten to 90% of the weight.

[0019] the molecular weight of (alpha) has the maximal value in molecular weight 1000-20000 in GPC -- desirable -- further -- desirable -- the maximal value -- 2000-19000 -- the maximal value is 3000-15000 especially preferably. Heat-resistant shelf life and a fine-particles fluidity improve by carrying out to 1000 or more, and a grindability improves by carrying out to 20000 or less. Moreover, it is 20 - 45% to contain THF insoluble matter five to 60% of the weight especially preferably 15 to 50% desirable still more preferably. Hot-proof offset nature improves by making

THF insoluble matter contain.

[0020] The following etc. are mentioned as an example of the toner binder of this invention.

\*\* The propylene oxide addition product / dodecenyl succinic acid / adipic-acid polycondensation object of the two mol addition product of bisphenol A propylene oxide / phenol novolak, The propylene oxide addition product / dodecenyl succinic acid / trimellitic anhydride polycondensation object of the two mol addition product of mixture \*\* bisphenol A propylene oxide / hydrogenation bisphenol A / phenol novolak of styrene / butadiene copolymerization object, Styrene / butadiene copolymerization object, and the propylene oxide addition product / adipic acid / sebacic-acid polycondensation object of mixture \*\* hydrogenation bisphenol A / phenol novolak of polystyrene, The propylene oxide addition product / dodecenyl succinic acid / trimellitic anhydride polycondensation object of the two mol addition product of mixture \*\* bisphenol A propylene oxide / hydrogenation bisphenol A / phenol novolak of styrene / stearyl metaacrylate copolymer In the propylene oxide addition product / dodecenyl succinic acid / maleic anhydride / trimellitic anhydride polycondensation object of the two mol addition product of mixture \*\* bisphenol A propylene oxide / phenol novolak of a styrene polymer, and a styrene / butadiene copolymer In the propylene oxide addition product / dodecenyl succinic acid / maleic anhydride / trimellitic anhydride polycondensation object of the two mol addition product of thing \*\* bisphenol A propylene oxide / hydrogenation bisphenol A / phenol novolak which carried out graft polymerization, styrene What carried out the graft polymerization of the styrene, Mixture \*\* hydrogenation bisphenol A / sebacic acid / trimellitic anhydride polycondensation object, and styrene/glycidyl methacrylate of styrene / stearyl metaacrylate copolymer A pile The polycondensation object of propylene oxide addition product / dodecenyl succinic-acid/(styrene / maleic-acid monobutyl copolymer) of reactant \*\* hydrogenation bisphenol A / phenol novolak of \*\*\*\* [0021] The manufacture approach of the toner binder of this invention is illustrated. Polyester (A1) is obtained by heating polycarboxylic acid and polyol at 150-280 degrees C under existence of well-known esterification catalysts, such as tetrabutoxy titanate and Djibouti rutin oxide, and carrying out dehydration condensation. In order to raise the reaction rate of the reaction last stage, it is also effective to make it reduced pressure. Vinyl system resin (B1) copolymerizes a configuration monomer by the well-known radical initiator, and is obtained. As a radical initiator, azo system initiators (azobisisobutyronitril, azobisvaleronitrile, etc.), peroxide system initiators (benzoyl peroxide, t-butyl par benzoate, di-t-butyl peroxide, G tert-butyl peroxide hexahydro terephthalate, etc.), etc. are mentioned. As a polymerization method, well-known polymerization methods, such as solution polymerization, bulk polymerization, a suspension polymerization, and an emulsion polymerization, can be used. As a solvent used in the case of solution polymerization, aromatic series solvents (toluene, xylene, etc.); ketones (acetone, methyl-ethyl-ketone, methyl-isobutyl-ketone, cyclohexanone, etc.); halogen system solvent; (dichloroethane etc.), amide system solvents (dimethylformamide etc.), etc. can be used. When a solvent is used, a solvent is distilled out under ordinary pressure and reduced pressure after a polymerization. When obtaining according to a suspension polymerization, a polymerization can be underwater carried out using organic system dispersants, such as a dispersant of inorganic systems, such as a calcium carbonate and calcium phosphate, or polyvinyl alcohol, and a methylation cellulose. Although polymerization temperature is chosen by the molecular weight of the radical initiator to be used and a toner binder, it is usually 50-170 degrees C preferably 5-200 degrees C. Polymerization time amount is usually 2 - 24 hours preferably for 1 to 48 hours. In the case of the mixture of (A) and (B), the manufacture approach of the compound-ized resin (alpha) can use any approaches, such as an existence Shimo polymerization method, solution alligation, melting alligation, and a powder-mixing method. By the existence Shimo polymerization method, it is obtained by carrying out the polymerization of the monomer of another side to the bottom of existence of (A) or (B). With solution alligation, (A) which carried out the polymerization separately, and (B) are obtained by distilling out a solvent after dissolving in a solvent usable to the solution polymerization of the above-mentioned vinyl resin, and the same solvent. melting alligation -- both a batch type and continuous system -- although -- it is applicable, and when it is continuous system, it is obtained by kneading at 100-230 degrees C using an extruder etc. In the case of a batch type, it mixes at 150-230 degrees C

in a reaction vessel etc. By the powder-mixing method, it is obtained by mixing the fine particles of each component using a NAUTA mixer, a Henschel mixer, etc. The resin in which (B) carried out the chemical bond to (A) can be manufactured by the following well-known approaches etc.

\*\* How to introduce the double bond and copolymerize the configuration monomer of this polyester and vinyl system resin by using a fumaric acid etc. into polyester.

\*\* How to carry out the polycondensation of the configuration monomer of vinyl system resin (obtained by copolymerizing a maleic anhydride, an acrylic acid, hydroxy methacrylate, etc.), and polyester which has a carboxyl group or a hydroxyl group.

\*\* How to carry out the polymer reaction of the vinyl system resin which has the hydroxyl group of polyester, a carboxyl group, and the functional groups (an acid-anhydride radical, an epoxy group, isocyanate radical, etc.) in which they and a reaction are possible.

[0022] The toner binder of this invention mixes various additives, such as a release agent and an electric charge control agent, etc. according to a coloring agent and the need, and is used as a dry type toner. A color well-known as a coloring agent, a pigment, and magnetic powder can be used. Specifically Carbon black, the Sudan black SM, the first yellow G Benzidine yellow, pigment yellow, India first Orange, IRUGASHIN red, rose nit aniline red, toluidine red, Carmine FB, Pigment Orange R, Lake Red 2G, Rhodamine FB, the Rhodamine B lake, A methyl-violet-B lake, a copper phthalocyanine blue, pigment blue, PURIRIANTO green, Phthalocyanine Green, the oil yellow GG, the kaya set YG, ora ZORU Brown B, the oil pink OP, magnetite, iron black, etc. are mentioned. The content of the coloring agent in a toner is usually 2 - 15 % of the weight, when using a color or a pigment, and when using magnetic powder, it is usually 20 - 70 % of the weight.

[0023] A thing well-known as a release agent can be used, for example, polyolefine WA@KKUSU (polyethylene wax, polypropylene wax, etc.); long-chain hydrocarbons (paraffin WA@KKUSU, SAZORU wax, etc.); carbonyl group content waxes (carnauba wax, a montan wax, distearyl ketone, etc.) etc. are mentioned. The content of the release agent in a toner is usually 0 - 10 % of the weight, and is 1 - 7 % of the weight preferably. As an electric charge control agent, a quarternary-ammonium-salt compound, the well-known thing, i.e., Nigrosine color, a quarternary-ammonium-salt radical content polymer, metal-containing azo dye, a salicylic-acid metal salt, a sulfonic group content polymer, a \*\* fluorine system polymer, a halogenation ring content polymer, etc. are mentioned. The content of the electric charge control agent in a toner is usually 0 - 5 % of the weight. Furthermore, a plasticizer can also be used. As a plasticizer, well-known things, such as colloidal silica, alumina powder, titanium oxide powder, and calcium-carbonate powder, can be used.

[0024] The well-known kneading grinding method etc. is mentioned as a manufacturing method of a dry type toner. After carrying out the dry type blend of the above-mentioned toner component, melting kneading is carried out, it pulverizes after that using a jet mill etc., pneumatic elutriation is carried out further, and it is obtained as a particle whose particle size is usually 2-20 micrometers.

[0025] It is mixed with carrier particles, such as a ferrite which coated the front face if needed with iron powder, a glass bead, nickel powder, a ferrite, magnetite, and resin (acrylic resin, silicone resin, etc.), and the dry type toner using the toner binder of this invention is used as a developer of an electric latent image. Moreover, it can rub against members, such as an electrification blade, instead of a carrier particle, and an electric latent image can also be formed. Subsequently, it is fixed to base materials (paper, polyester film, etc.) by the well-known hot calender roll fixing approach etc., and considers as a record ingredient.

[0026] Although an example explains this invention further below, this invention is not limited to this. Hereafter, the section shows the weight section.

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[Translation done.]

## \* NOTICES \*

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1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.\*\*\*\* shows the word which can not be translated.

3.In the drawings, any words are not translated.

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## EXAMPLE

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[Example]

[0027] The measuring method of the property of the toner binder obtained in the example and the example of a comparison is shown below.

1. The acid number and hydroxyl value JIS The approach of the convention to K0070.

In addition, when the solvent insoluble matter accompanying bridge formation was in a sample, the thing after melting kneading was used as a sample by the following approaches.

Kneading equipment : Product made from an Oriental energy machine Lab PURASUTO mill

MODEL30R150 kneading conditions : It is a 30-minute 2. glass transition point (T<sub>g</sub>) at 130 degrees C and 70rpm.

ASTM The approach of the convention to D 3418-82 (DSC law).

Equipment: Product made from SEIKO Electronic industry SSC / DSC20 and 5803. molecular weight THF extractives is measured with gel permeation chromatography (GPC). The conditions of the determination of molecular weight by GPC are as follows.

Equipment : Product made from Oriental soda HLC-802A column : TSK GEL GMH6 Two (product made from Oriental soda)

Measurement temperature : 25-degree-C sample solution : 0.25% of the weight of tetrahydrofuran solution solution injection rate: 200microl detection equipment : The refractive index detector, in addition the molecular-weight calibration curve were created using standard polystyrene.

4. Add 50ml THF to 0.5g of tetrahydrofuran (THF) insoluble matter samples, and carry out stirring reflux for 3 hours. Insoluble matter is carried out a \*\* exception with a glass filter after cooling, and reduced pressure drying is carried out at 80 degrees C for 3 hours. Insoluble matter is computed from the weight ratio of the weight of the pitch on a glass filter, and a sample.

5. Measurement of dielectric dissipation factor (tandelta) Equipment : Ando Electric Co., Ltd. make TR-1100 mold dielectric loss measuring device Electrode : Ando Electric Co., Ltd. make SE-43 mold What was ground to 20 micrometers or less was used as a sample after melting kneading by the following approaches of being a fine-particles electrode.

Kneading equipment : Product made from an Oriental energy machine Lab PURASUTO mill MODEL 30R150 Kneading conditions : It is 30 minutes at 130 degrees C and 70rpm. [0028] The two mol addition product 673 of bisphenol A propylene oxide section, the five mol addition product 15 of propylene oxide section of phenol novolak resin (the number of nuclides about five pieces), the terephthalic-acid 157 section, the maleic-anhydride 37 section, the dodecenyl succinic-acid anhydride 152 section, and the Djibouti rutin oxide 2 section were put in into the reaction vessel to which example 1 (composition of polyester) cooling pipe, an agitator, and nitrogen installation tubing were attached, and it reacted at 220 degrees C under ordinary pressure for 8 hours, and reacted by reduced pressure of further 10 - 15mmHg for 5 hours. subsequently, added the trimellitic anhydride 32 section to this, and it was made to react by 180-degree-C ordinary pressure for 2 hours, and came out, and polyester (A1) was obtained. (Composition of a toner binder) The xylene 450 section was put in into the autoclave reaction vessel to which the thermometer and the agitator were attached, and after the nitrogen purge, at 170 degrees C, the mixed liquor of the polyester (A1) 300 section, the styrene 651 section, the

butadiene 49 section, and the di-*t*-butyl peroxide 7 section was dropped in 2 hours, and carried out the polymerization. Subsequently, reduced pressure drying was carried out at 200 degrees C, and the toner binder (1) of this invention was obtained. For the THF insoluble matter of a toner binder (1), peak molecular weight was [ 62 degrees C and  $\Delta$  of 9500 and  $T_g$  ]  $2.0 \times 10^{-3}$  42%.

[0029] They are the two mol addition product 506 of bisphenol A propylene oxide section, and hydrogenation bisphenol A in the reaction vessel to which example 2 (composition of polyester) cooling pipe, an agitator, and nitrogen installation tubing were attached. The 87 sections, the five mol addition product 15 of propylene oxide section of phenol novolak resin (the number of nuclides about five pieces), the maleic-anhydride 29.5 section, the dodecenyl succinic-acid anhydride 394 section, and the Djibouti rutin oxide 2 section were put in, and it reacted at 220 degrees C under ordinary pressure for 8 hours, and reacted by reduced pressure of further 10 – 15mmHg for 5 hours. subsequently, added the trimellitic anhydride 28 section to this, and it was made to react by 180-degree-C ordinary pressure for 2 hours, and came out, and polyester (A2) was obtained.

(Composition of a toner binder) The xylene 320 section was put in into the autoclave reaction vessel to which the thermometer and the agitator were attached, and after the nitrogen purge, at 170 degrees C, the mixed liquor of the polyester (A2) 500 section, the styrene 500 section, and the di-*t*-butyl peroxide 5 section was dropped in 2 hours, and carried out the polymerization. Subsequently, reduced pressure drying was carried out at 200 degrees C, and the toner binder (2) of this invention was obtained. For the THF insoluble matter of a toner binder (2), peak molecular weight was [ 60 degrees C and  $\Delta$  of 11000 and  $T_g$  ]  $1.9 \times 10^{-3}$  38%.

[0030] After putting in the water 2000 section and the polyvinyl alcohol 3 section into the autoclave reaction vessel to which example 3 (composition of styrene resin) thermometer and the agitator were attached and dissolving enough, the mixed monomer of the styrene 850 section and the butadiene 150 section and the G tert-butyl peroxide hexahydro terephthalate 2 section were added to this, and the suspension polymerization was carried out at 95 degrees C after that by 85 degrees C after the nitrogen purge for 3 hours for 10 hours. After cooling, the \*\* exception, the reactant was rinsed, was dried at 50 degrees C, and styrene resin (B1) was obtained.

(Composition of polyester) like the example 1, hydrogenation bisphenol A was made to react at 220 degrees C, having used the Djibouti rutin oxide 2 section as the catalyst for the 501 sections, the sebacic-acid 127 section, the maleic-anhydride 10.4 section, and the dodecenyl succinic-acid anhydride 371 section, it came out of it, and polyester (A3) was obtained.

(Composition of a toner binder) The xylene 250 section was put in into the autoclave reaction vessel to which the thermometer and the agitator were attached, and after the nitrogen purge, at 170 degrees C, the mixed liquor of the polyester (A3) 400 section, the styrene 400 section, and the di-*t*-butyl peroxide 12 section was dropped in 2 hours, and carried out the polymerization. Subsequently, the styrene resin (B1) 200 section and the xylene 750 section were added, after carrying out dissolution distribution, reduced pressure drying was carried out at 200 degrees C, and the toner binder (3) of this invention was obtained. For the THF insoluble matter of a toner binder (2), peak molecular weight was [ 63 degrees C and  $\Delta$  of 7100 and  $T_g$  ]  $2.3 \times 10^{-3}$  23%.

[0031] The two mol addition product 348 of bisphenol A propylene oxide section, the two mol addition product 320 of bisphenol A ethyleneoxides section, the terephthalic-acid 166 section, the fumaric-acid 62.5 section, the anhydrous dodecenyl succinic-acid 54 section, the hydroquinone 0.1 section, and the Djibouti rutin oxide 2 section were put in into the reaction vessel to which example of comparison 1 cooling pipe, an agitator, and nitrogen installation tubing were attached, and it reacted at 230 degrees C under ordinary pressure for 12 hours, and reacted by reduced pressure of further 10 – 15mmHg for 3 hours. Subsequently, add the trimellitic anhydride 64 section and it was made to react by reduced pressure of 10 – 15mmHg, when the acid number was set to 20, it took out from the reaction vessel, and polyester (A4) was obtained. The THF insoluble matter of (A4) was 32%, peak molecular weight was 6200,  $T_g$  was 59 degrees C and  $\Delta$  was  $1.2 \times 10^{-2}$ . Let polyester (A4) be a comparison toner binder



(1).

[0032] Except changing example of comparison 2 (composition of styrene resin) monomer into the styrene 720 section and the butyl acrylate 280 section, the polymerization was carried out like the styrene resin (B1) of an example 3, and resin (B-2 -1) was obtained. The xylene 450 section was put in into the autoclave reaction vessel to which the thermometer and the agitator were attached, and after the nitrogen purge, at 170 degrees C, the mixed liquor of the mixed monomer of the styrene 870 section and the butyl acrylate 130 section and the di-t-butyl peroxide 15 section, and the xylene 120 section was dropped in 3 hours, and carried out the polymerization. Subsequently, desolventization was carried out and resin (B-2 -2) was obtained. The resin (B-2 -1) 300 section and the resin (B-2 -2) 700 section were added to the xylene 1000 section, and it was made to dissolve in the bottom of reflux. Subsequently, reduced pressure drying was carried out at 180 degrees C, and styrene resin (B-2) was obtained. (Composition of a toner binder) After carrying out powder mixing of the polyester (A4) 500 section and the styrene resin (B-2) 500 section, it kneaded with the 2 shaft kneading machine (IKEGAI Make PCM-30), and the comparison toner binder (2) was obtained. tandelta of a comparison toner binder (2) was  $6.1 \times 10^{-3}$ .

[0033] To toner binder [ of the examples 1-3 of evaluation and the example 1 of comparative evaluation, and 2 this invention ] (1) - (3), and the comparison toner binder (1) (2) 100 section, the magnetic powder (Toda Kogyo Corp. make EPT-1000) 100 section, the low-molecular-weight-polypropylene ( [ by Sanyo Chemical Industries, Ltd. ] bis-call 550 P) 4 section, and the electric charge control agent T-77 (Hodogaya chemistry (\*\*)) 0.8 section were added, and it toner-ized by the following approach. First, after carrying out preliminary mixing using a Henschel mixer ( FM10made from Mitsui Miike Chemically-modified Opportunity B), it kneaded with the 2 shaft kneading machine (IKEGAI Make PCM-30). Subsequently, after pulverizing using supersonic jet grinder lab jet (product made from Japanese Pneumatic Industry), it classified with the air-current classifier ( MDS-I made from Japanese Pneumatic Industry), and the toner particle whose particle size d50 is 8 micrometers was obtained. Subsequently, the colloidal silica (Aerosil R972: product made from Japanese Aerosil) 1 section was mixed with the sample mill in the toner particle 100 section, and toner (1) - (3) comparison toner (1) and (2) were obtained. An evaluation result is shown in Table 1.

[0034]

[Table 1]

concentration (H/H) MFT HOT		Toner No Image concentration (N/N) Image	
130 degrees C	220 degrees C	Toner (2) 1.55 1.37	125 degrees C 230 degrees C Toner (3) 1.54
1.31	125 degrees C	220 degrees C Comparison toner (1) 0.82 0.64	125 degrees C 200 degrees C
Comparison toner (2) 1.28	0.85	130 degrees C	190 degrees C

----- [The evaluation approach]

\*\* The black solid image was printed using the image concentration marketing laser printer (LBP-210; Canon make), and the image concentration was measured using the Macbeth concentration meter. Let what performed what developed negatives by ordinary temperature normal relative humidity (23 degrees C, 50%RH) with image concentration (N/N) and high-humidity/temperature (35 degrees C, 85%RH) be image concentration (H/H).

\*\* The fixing unit of a commercial copying machine (SF8400A; Sharp make) was converted, and the paper feed rate evaluated the non-established image developed using the minimum fixing temperature (MFT) marketing laser beam printer (LBP-210; Canon make) using the fixing machine adjustable in 160 mm/sec and fixing temperature. The survival rate of the image concentration after grinding a fixing image against putt considered as the minimum fixing temperature with the fixing roll temperature used as 70% or more.

\*\* Fixing evaluation was carried out like the hot offset generating temperature (HOT) above MFT, and visual evaluation of the existence of the hot offset to a fixing image was carried out. It considered as hot offset generating temperature with the fixing roll temperature which hot offset generated.

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[Translation done.]